

PATENT SPECIFICATION

NO DRAWINGS

1,000,477

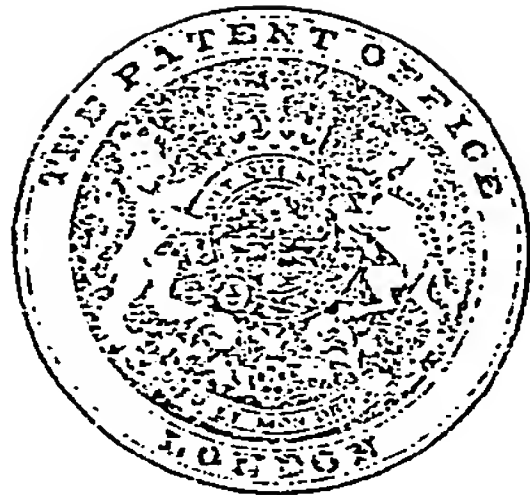
Date of Application and filing Complete Specification: Aug. 7, 1962.

No. 30253/62.

Application made in United States of America (No. 129,968) on Aug. 8, 1961.

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Index at acceptance:—C2 C(P1L1, P1L2, P3B11A, P3B12A, P3B12B, P3B14B, P3B17, P3B18B, P3B18C, P3B18D, P3B19C, P3B19E, P3B20, P3B P4, P5B, P7); C2 J(1, 2); C5 E(B2E1, B2M1); C7 F(1B2, 1B4, 4H)

Int. Cl.:—C 07 f // C 07 c, C 23 c

COMPLETE SPECIFICATION

Improvements in the Production and use of Organo Nickel Complexes, containing Phosphorus, Arsenic or Antimony

SPECIFICATION NO. 1,000,477

By a direction given under Section 17(1) of the Patents Act 1949 this application proceeded in the name of COLOMBIAN CARBON COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of 380, Madison Avenue, New York, State of New York, United States of America.

THE PATENT OFFICE

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- 15 four atoms of the elements phosphorus, arsenic, and/or antimony, the bonding being directly to said element with organic radicals also being bonded directly to said element or through oxygen, particularly tetrakis(triorganophosphite) nickel complexes.

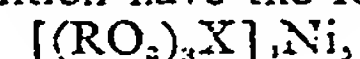
- 20 The resulting compounds or complexes are useful as catalysts for organic reactions, such as the polymerization or oligomerization of olefins, and particularly for preparing cyclo-oligomers of open chain conjugation diolefins.
- 25 The cyclic products may have from eight to twenty carbon atoms in the ring with a carbon to carbon double bond for each molecule of diolefin incorporated therein. Cyclic compounds with side chains are also produced. Of particular value is the use of the compounds of the invention to catalyze the reaction of 1,3-butadiene to give 1,5 - cyclooctadiene, 1,5,9-cyclododecatriene and to some extent various *cis*,
- 30 *trans* and *cis-trans* isomers thereof. In some cases, the nickel compounds of the invention may be thermally decomposed to give finely divided nickel or coatings of metallic nickel.

- 35 The nickel compounds obtained by the process of the invention and methods of using
- 40 [Price 4s. 6d.]

starting material is nickel carbonyl, which presents hazards in handling.

The preferred embodiments of the present invention avoid these problems and provide an alternative method of preparing the subject complexes. It has now been discovered that inexpensive divalent and trivalent nickel compounds which in most cases are commercially available at reasonable cost, and in forms which are relatively safe to handle, are useful for the preparation of the subject coordination compounds. However, less preferred embodiments of the present invention advantageously include the use of the divalent and trivalent organonickel compound starting materials of the latter of these aforesaid Specifications, an advantage being that a smaller amount of the phosphorus, arsenic, or antimony compound is required and/or less severe conditions are required. Also within the invention is the method of using these compounds as catalysts for the cyclooligomerization of olefins.

The tetrasubstituted, trisubstituted, and disubstituted nickel compounds prepared according to the invention have the formulae:



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Int. Cl.:—C 07 f // C 07 c, C 23 c

COMPLETE SPECIFICATION

Improvements in the Production and use of Organo Nickel Complexes, containing Phosphorus, Arsenic or Antimony

We, CITIES SERVICE RESEARCH AND DEVELOPMENT COMPANY, a corporation organized and existing under the laws of the State of New Jersey, United States of America of Sixty Wall Tower, 70 Pine Street, New York 5, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of preparing substituted coordination compounds of nickel in which the nickel atom is bonded to four atoms of the elements phosphorus, arsenic, and/or antimony, the bonding being directly to said element with organic radicals also being bonded directly to said element or through oxygen, particularly tetrakis(triorganophosphite) nickel complexes.

The resulting compounds or complexes are useful as catalysts for organic reactions, such as the polymerization or oligomerization of olefins, and particularly for preparing cyclo-oligomers of open chain conjugation diolefins. The cyclic products may have from eight to twenty carbon atoms in the ring with a carbon to carbon double bond for each molecule of diolefin incorporated therein. Cyclic compounds with side chains are also produced. Of particular value is the use of the compounds of the invention to catalyze the reaction of 1,3-butadiene to give 1,5 - cyclooctadiene, 1,5,9-cyclododecatriene and to some extent various *cis*, *trans* and *cis-trans* isomers thereof. In some cases, the nickel compounds of the invention may be thermally decomposed to give finely divided nickel or coatings of metallic nickel.

The nickel compounds obtained by the process of the invention and methods of using

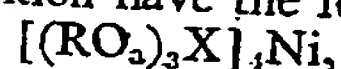
[Price 4s. 6d.]

them are in part disclosed in our Specifications Nos. 19420/61 Serial No. 971,755 and 19421/61 (Serial Nos. 971,771 and) filed May 30, 1961.

The new method of preparation of such compounds by the process disclosed herein possesses a number of advantages over prior methods. The earlier methods often require the use of expensive or quite toxic compounds of nickel, as starting materials. Thus, one method involves the use of bis(cyclopentadienyl) nickel and similar organo-metallic compounds which at present are not commercially available at reasonable prices. Another known starting material is nickel carbonyl, which presents hazards in handling.

The preferred embodiments of the present invention avoid these problems and provide an alternative method of preparing the subject complexes. It has now been discovered that inexpensive divalent and trivalent nickel compounds which in most cases are commercially available at reasonable cost, and in forms which are relatively safe to handle, are useful for the preparation of the subject coordination compounds. However, less preferred embodiments of the present invention advantageously include the use of the divalent and trivalent organo-nickel compound starting materials of the latter of these aforesaid Specifications, an advantage being that a smaller amount of the phosphorus, arsenic, or antimony compound is required and/or less severe conditions are required. Also within the invention is the method of using these compounds as catalysts for the cyclooligomerization of olefins.

The tetrasubstituted, trisubstituted, and disubstituted nickel compounds prepared according to the invention have the formulae:



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- and $[(RO)_3X]_2Ni(XR^{11})_2R^1$
 $[R^1(R^{11})_2X]_2Ni$
- in which each R, R¹, and R¹¹ is a hydrocarbon radical or an acyl or halogen derivative thereof, α is one or zero, and X is phosphorus, arsenic, or antimony. It is believed that the nickel in these complexes is zero-valent and is attached to the ligands by co-ordination bonds.
- The method according to the invention of preparing such compounds comprises reacting (1) a nickel compound having a valency (covalency or electrovalency) of 2 or 3 with (2) a ligand or mixture of ligands of the formula
- $(RO)_3X$,
- in the presence of (3) a reducing agent selected from organometallic compounds, organometallic halides, metal hydrides, and organometallic hydrides, alkali metal ethoxides, metallic reducing agents more positive than nickel hydrazine, alkyl hydrazines, carbonyl hydrides, organic phosphines, organic phosphites and hydrogen.
- The ligand is preferably a triorganophosphite, although it may also be a triorganophosphine, triorgano-arsenite, triorganoarsine, triorganoantimonite, or triorganostibine. The ligand may contain two atoms of phosphorus, arsenic, or antimony, as in the last two of the three formulae given above (ditertiary compounds), otherwise being similar to the preferred ligand. Examples of this type of ligand are orthophenylenebisdimethylarsine, orthophenylene-bisdimethylphosphine, propylenebisdimethylphosphine, and orthophenylenebisdimethylstibine. These ligands are suitably prepared by the methods of Chatt et al, U.S. Patent Specification No. 2,922,819.
- The radical R in the ligand is a hydrocarbon or a halogen- or acyl-substituted hydrocarbon radical. Examples of suitable hydrocarbon radicals include: open-chain alkyl radical preferably having less than about 20 carbon atoms, such as methyl, ethyl, propyl, butyl, hexyl, dodecyl, isooctyl, isobutyl and isopentyl; cycloalkyl radicals including cyclopentyl, cyclohexyl and cyclooctyl; and aryl radicals such as phenyl, biphenyl, α-naphthyl, and β-naphthyl; alkylaryl radicals such as *m*-tolyl, *p*-tolyl, *o*-tolyl, and 3,5-xyl; and arylalkyl radicals such as the benzyl and benzo hydryl radicals.
- The halogen substituent can be chlorine, fluorine, bromine or iodine. Examples of halogen-substituted radicals are *p*-chlorophenyl, 2-chloroethyl, *m*-(trifluoromethyl) phenyl, and bromocyclohexyl radicals. A useful acyl-substituted hydrocarbon radical is *p*-acetophenyl.
- The radicals R may be identical or different. Examples of compounds wherein the radicals are the same are tetrakis (triphenylphosphite) nickel; tetrakis (tri-*p*-tolyl-phosphite) nickel; tetrakis (triphenylphosphine) nickel; tetrakis (tricyclohexylphosphite) nickel. Instances of catalysts containing differing radicals R are tris (triphenylphosphite) tri-*p*-tolylphosphite nickel; and tris (triphenylphosphite) triethylphosphite nickel. Similar variations may be made where phosphine compounds are utilized, and both phosphine and phosphite compounds may be bonded to the Ni⁰. Comparable tetrasubstituted compounds, but with arsines, arsenites, stibines, and/or antimonites substituted for the phosphines and phosphites are within the invention.
- The radicals R¹ are preferably arylene and less desirably alkylene, and the radicals R¹¹ are preferably alkyl radicals. In general, the radicals R¹ and R¹¹ are similar to the radicals R. Suitable as the radical R¹ are phenylene, tolylene, naphthalene, and substitution products thereof, the *o*-arylene radicals being preferred, or alkylene radicals such as ethylene and propylene. The radicals R¹¹ are suitably ethyl, methyl, propyl, butyl, or halogen-substituted alkyl such as chloroethyl.
- The nickel compound useful as the starting material may contain nickel in a valence state of from two to three. Preferably the nickel is divalent.
- Suitable preferred divalent nickel compounds as the starting material include nickel chloride, nickel bromide, nickel iodide, nickel cyanide, nickel mono-oxide, nickel carbonate, nickel fluoride, nickel sulfate, and nickel monosulfide, preferably having no water of crystallization or hydration. Nickel dihalides are especially preferred. Similar trivalent nickel compounds, e.g., nickel sesquioxide (Ni₂O₃), and nickelic hydroxide [Ni(OH)₂] are of benefit. Also, Werner complexes, such as Ni(NH₃)₆Cl₂ are useful.
- Carboxylic acid salts of divalent nickel are useful, including nickel acetate, nickel propionate, nickel caprylate, nickel oleate, nickel lactate, nickel citrate, nickel benzoate, nickel salicylate, and nickel naphthenate. Also suitable are nickel petroleum sulfonate, nickel 2-ethylhexylsulfate, nickel dilaurylphosphate, nickel ethylxanthate, nickel dimethyldithiocarbamate, nickel phenyldithiocarbamate, nickel dithiocarbanilate, nickel bis(*p*-octylphenol) sulfide, nickel acetylacetonate, nickel ethylenediamine - bis - acetylacetonate, nickel dimethylglyoxime, and nickelpthalocyanine. The carboxylic acid salts and chelates of nickel give excellent results, the inorganic nickel compounds being preferred from the standpoint of cost, however. It is to be noted that the organic derivatives of nickel recited immediately above are not organonickel compounds in which the nickel is attached directly to at least one organic carbon atom, by ionic or ionic and coordination bonds, but that both classes of compounds are useful. For suitable organonickel compounds of this latter type as starting

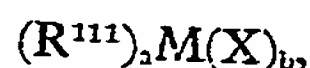
materials, the nickel being divalent or trivalent, reference is made to our Specification No. 19421/61 Serial No. 971,771. By way of example, such compounds include bis (cyclopentadienyl) nickel, bis(methylcyclopentadienyl) nickel, bis(indenyl) nickel, and bis(acrylonitrile) nickel.

The reducing agents may be referred to as "external reducing agents", since they are reducing compounds or reducing materials other than the ligand, although they may be of the same general type, for instance, in the case where triisopropyl phosphite is utilized as the external reducing agent for the preparation of tetrakis(triphenylphosphite) nickel from nickel naphthenate and triphenylphosphite. Generally, the external reducing agent should be chosen such that it complexes, if at all, with nickel less strongly than the selected ligand, it does not enter into markedly competing reactions for the ligand or for nickel, and it is non-destructive of the ligand and the product.

The preferred reducing agents are of the type used in the preparation of "Ziegler" polymerization catalysts, that is, a hydride, organometallic compound, organometallic hydride, or organometallic halide of a non-transition metal selected from the metals of periodic groups IA, IIA, IIB, IIIA, and IVA. The particularly preferred metals are Al, Li, Na, K, Mg, Cd, Ba, Zn, Ca, Hg, Sn, and Pb. These elements have an atomic weight no higher than 208, and have a maximum valence state of +4. Specifically group IIIA is preferred, and particularly aluminum.

In this specification, the periodic chart or table of the elements appearing in *Fundamental Chemistry*, 2nd Edition, by H. G. Deming, John Wiley and Sons, is the one referred to. This table is reprinted in *Lange's Handbook of Chemistry* 7th Ed., Handbook Publisher's, Inc., Sandusky, Ohio, 1949, at pages 58 and 59. This is the "long" or "Bohr" table.

The non-transition metal compound useful as the reducing agent in the preparation of the catalyst has the characteristic formula

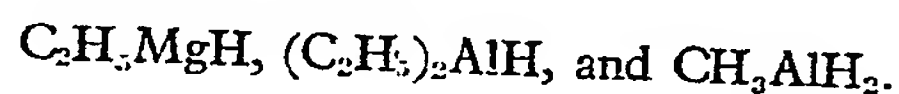


wherein "M" is a nontransition metal as defined above, R^{111} is a hydrocarbon or hydrogen radical, "X" is a halide radical, and "a" and "b" are numbers the sum of which is equal to the valences of the metal, with the proviso that "a" is always 1 or more. Where "a" is more than one, and "b" equals zero R^{111} may include both hydrocarbon and hydrogen radicals, as in the organometallic hydrides. When R^{111} is exclusively hydrogen, "b" equals zero. Different hydrocarbon and different halogen radicals may be attached to the same metal atom. Complexes having atoms of different metals are included. In the description and claims of this specification, the term "Ziegler reducing agents" is intended to denote the preferred

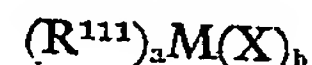
reducing agents as defined above, specific examples of which follow.

Examples of compounds in which R^{111} is exclusively a hydrocarbon radical are: triethyl aluminum, tributyl aluminum, triisobutyl aluminum, diethyl isobutyl aluminum, trihexyl aluminum, tridodecyl aluminum, triphenyl aluminum, ethyl dibenzyl aluminum, triheptyl aluminum, and tricyclohexyl aluminum. Other examples of suitable radicals R^{111} include methyl, amyl, propyl, isopropyl, octyl, and tolyl. Preferably the organo or hydrocarbon radical R^{111} is a straight or branched chain alkyl radical, although it may be alkylene, cycloalkyl, arylalkyl, or alkylaryl. The radicals R^{111} may be similar for the compounds which also have hydrogen or halogen radicals attached to the metal atom, the organo-metallic hydrides and the organometallic halides. Similar organometallic compounds of the metals other than aluminum are useful, examples being ethyl lithium, allyl sodium, phenyl sodium, butyl potassium, diethyl calcium, dibutyl zinc, sodium aluminum tetraethyl, and tetraethyl lead.

The hydrides useful according to this invention include the following representative examples: LiH , NaH , KH , MgH_2 , BaH_2 , ZnH_2 , CdH_2 , HgH_2 , HgH , AlH_3 , SnH_4 , PbH_4 , and mixed hydrides of the above such as $LiAlH_4$. Examples of useful organometallic hydrides are:



Organometallic halides within the above formula



include the following examples: C_6H_5MgBr and other Grignards reagents,



Useful halogens include chlorine, bromine, fluorine, and iodine.

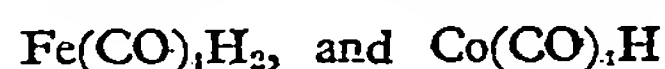
In addition to or in place of the above-defined "Ziegler" type of reducing agent, others may be used, for instance, metallic reducing agents more electropositive than nickel are suitable. Examples of such metallic reducing agents include zinc, aluminum, magnesium, iron, and sodium, alloys of the preceding such as of zinc and aluminum, and alloys or mixtures with the hydrides mentioned heretofore. An example of the latter is a mixture or alloy of metallic aluminum and aluminum hydride.

Organic phosphines and phosphites having a lesser affinity for nickel than the desired ligand are also useful as the external reducing agent, although cost may discourage the use of such compounds.

Alkali metal ethoxides, such as sodium or

potassium ethoxide, are useful in some cases, as where phosphines comprise the ligands to be complexed with nickel. With other ligands, such as the triorganophosphites, transesterification may result, and thus the alkali metal alcoholates, though operable as the reducing agent even with the phosphites, are not preferred with such ligands.

Hydrazine and substituted hydrazines such as methyl hydrazine, dimethyl hydrazines, ethyl hydrazine, propyl hydrazine, and phenyl hydrazine are suitable reducing agents, as are hydrogen, and metal carbonyl hydrides such as



which, however, decompose at relatively low temperatures.

The quantity of reducing agent depends upon its nature, and the nature of the nickel compound used as a starting material. The amount of reducing agent used in each case is not particularly critical but should be an amount not lower than that necessary to reduce the nickel, such as in nickel chloride, to the zero-valent state. If a material other than the nickel compound is present which will react with or complex with the reducing agent, an excess of the reducing agent is useful to fulfill this requirement.

Solvents are beneficial in some instances. However, they should be inert with respect to the ligand, the reducing agent, and the disubstituted, trisubstituted, or tetrasubstituted nickel complex. The ligand itself such as triphenylphosphite, may serve as solvent, as disclosed in said Specification No. 19421/61 Serial No. 971,771 filed May 30, 1961. Hydrocarbons such as benzene, petroleum naphtha, hexane, methylcyclohexane, xylene, decahydronaphthalene, and toluene are useful, as are tetrahydrofuran and ethyl ether. Water and ethanol or other alcohols are reactive with aluminum triethyl, for example, and are not of benefit in most instances.

The relative proportions of ligand and nickel compound in the reaction mixture should be such that approximately four moles of phosphorous, arsenic, and/or antimony per mole of nickel are present. The ratio of phosphorous, arsenic, and/or antimony to nickel in the reaction mixture may be less than four, but a lower yield of the desired product is obtained. An excess of ligand is useful, although the economic advantage attained by the use of an external reducing agent is diminished. The mole ratio of phosphorous, arsenic, and/or antimony to nickel suitably ranges between 4 to 1 and 20 to 1.

The temperature to which the ligand, the nickel compound, and the external reducing agent, with or without added solvent are subjected, varies widely, and depends in part upon the specific reactants used. In some instances, stepwise elevation of the temperature is bene-

ficial. In general, temperatures of from $-80^\circ\text{C}.$ to $250^\circ\text{C}.$ are useful. Preferred temperatures are from $25^\circ\text{C}.$ to $100^\circ\text{C}.$ The time of reaction is largely a function of temperature and may vary from 0.1 hours to 20 hours or longer if desired. Pressures depend in part upon the nickel compound, as well as the other components of the reaction mixture. Where volatile by-products are obtained, reduced pressures, as low as about 20 mm., are of benefit in some cases. Corrosive or deleterious by-products may be controlled by including a suitable reactant in the mixture. For instance, where hydrogen chloride is a by-product, triethyl amine or pyridine is useful to neutralize this product. In adding such materials, attention should be given to the severity of the reducing conditions; under severe conditions, pyridine is preferred to triethyl amine. Where a component of the reaction mixture is quite volatile, such as in the use of hydrogen gas as the reducing agent, higher pressures, in the neighbourhood of 140 kilograms per square centimeter gage are permissible. Ordinarily, ambient temperatures and pressures are satisfactory.

In preparing the nickel complexes, the reactants may be added in any order. Convenience or the nature of the materials may suggest a particular order, as where a vigorous reaction is controlled by the gradual or stepwise addition of a component. In Example 2, the trialkyl aluminum reducing agent was gradually added to the other reactants, with good results. Gaseous materials are conveniently added to the other reactants. Where different ligands are associated with the same molecule of nickel, such ligands may be added to the reaction mixture separately or together. Vigorous agitation is often of benefit.

An inert or non-oxidizing atmosphere is used, argon, nitrogen, and helium being useful. Of course, where the reducing agent is a gas or vapor such as hydrogen, the reaction zone is purged of air and the hydrogen provides the non-oxidizing atmosphere. Although the crude reaction mixture is active as the catalyst and may be prepared in the reactor in which it is to be used as a catalyst, it is preferred to isolate the active principal, as by washing with alcohol and acetone. Recrystallizing from benzene or tetrahydrofuran is sometimes useful.

The method of carrying out the preparative reaction according to the invention is illustrative by the following Examples Nos. 1 to 13. All parts are by weight and ambient temperatures and pressures were used, unless specified otherwise.

EXAMPLE 1

Into a 500 ml. flask, 5 grams of nickel bromide, and 100 ml. of anhydrous cyclohexane were placed. This was heated to $65^\circ\text{C}.$ and 30 grams of triphenylphosphite was added followed by 50 ml. of 10% by weight of tri-

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ethylaluminum in cyclohexane. This mixture was heated at 65° for 1 hour after which 10 cc of alcohol was added to destroy any triethylaluminum present. After cooling and removing the solvent, the residue was dissolved in tetrahydrofuran (THF) and filtered. The THF was removed by vacuum and 100 ml. of methyl alcohol added which caused a white precipitate to form. Filtering gave 6.5 grams of tetrakis (triphenylphosphite) nickel — m.p. 146—8°C., the yield being 21.8%.

EXAMPLE 2

A mixture, of 5 grams nickel acetylacetonate, 100 ml. benzene, and 28 grams tri (2 - chloroethyl) phosphite, was stirred under argon. To this was added dropwise 30 ml. of 10% triethylaluminum in benzene and the stirring continued for one hour. At the end of this, 150 ml. of methyl alcohol was added, which precipitated 19.2 grams (yield 75.2%) of a white solid, tetrakis [tri(2-chloroethyl) phosphite] nickel — m.p. 138—140°C.

EXAMPLE 3

A mixture of 5 grams of anhydrous nickel chloride, 100 grams of triphenylphosphite, and 3 grams of powdered iron was stirred for 16 hours at 200°C. while an inert atmosphere was maintained. No extraneous solvent was used. The reaction mixture was cooled to room temperature, and 150 ml. of methyl alcohol was added which precipitated about 20 grams of a dark colored solid. The solid was dissolved in tetrahydrofuran, filtered to remove the insoluble material, e.g., iron, and methyl alcohol was added to precipitate a white solid, tetrakis (triphenylphosphite) nickel with a melting point of 146—148°C. The yield was approximately 39%.

EXAMPLE 4

A mixture of 5 grams of anhydrous nickel chloride, 100 grams of triphenylphosphite, and 20 grams of triethyl amine was added to a 500 ml. autoclave. After addition of the mixture, the head of the autoclave was put into place and the autoclave was evacuated to remove the air. The reaction was carried out at 130°C. with a hydrogen pressure of 119

kilograms per square centimeter gage with a residence time of 1.5 hours. After cooling to room temperature, the hydrogen was vented off and the autoclave head was removed. Then 200 ml. of acetone was added to the reaction mixture and a dark solid was precipitated. The dark solid was dissolved in hot benzene, filtered to remove the insoluble material, and methyl alcohol was added which precipitated 2.1 grams of a white solid, tetrakis (triphenylphosphite) nickel, m.p. 146—148°C.

EXAMPLE 5

To 26.0 grams of a nickel naphthenate containing 6% nickel, 33.0 grams of triphenylphosphite was added, along with 5.5 grams of triisopropylphosphite, the latter serving as the external reducing agent. The resulting mixture was stirred at 130°—140°C. for 1.5 hours, then cooled to 30°C. with continued stirring, and 100 ml. of n-heptane was added to precipitate the product. The precipitate then was washed with methyl alcohol, leaving a residue of 4.4 grams of tetrakis(triphenylphosphite) nickel, a yield of 12.8%, as a very fine white powder.

EXAMPLE 6

To 26.0 grams of a nickel naphthenate containing 6% nickel, and 10 grams of n-heptane, a total of 33 grams of triphenylphosphite and 20 ml. of triethylaluminum in decahydronaphthalene, containing a total of 1.8 grams of triethylaluminum, was added under an inert atmosphere. These were stirred together for about 3 hours in the range 25°—35°C., and the temperature finally raised to 65°—75°C. for an additional hour. The mixture was allowed to cool slowly to room temperature, and 100 ml. of n-heptane was stirred in followed by 50 ml. of isopropyl alcohol. The precipitated tetrakis (triphenylphosphite) nickel was removed by filtration, washed well with methyl alcohol, air dried, and found to weigh 5.8 grams, a yield of 17%.

The examples set forth in the following table were conducted similarly to those given above.

TABLE I

Example	7	8	9	10	11	12	13
Nickel Compound and Amount	NiBr ₂ 4 g.	Nickel acetyl-acetate 5 g.	Nickel acetyl-acetate 5 g.	Nickel acetyl-acetate 5 g.	Nickel acetyl-acetate 5 g.	Nickel acetyl-acetate 5 g.	NiCl ₂ 5 g.
Reducing Compound and Amount	Triethyl Aluminum 0.6 g.	Triethyl Aluminum 1.2 g.	Triethyl Aluminum 3 g.	Triethyl Aluminum 3 g.	Triethyl Aluminum 3 g.	Triethyl Aluminum 3 g.	Phenyl-magnesium bromide 10 ml. 3 M Solution
Ligand and Amount	Triphenyl phosphite 20 g.	Triphenyl phosphite 30 g.	Tri(p-methoxy-phenylphosphite) 35 g.	Triphenyl phosphite 25 g.	Tridecyl phosphite 41 g.	Diphenyldecyl phosphite 30 g.	Triphenyl phosphite 40 g.
Solvent and Amount	Cyclohexane 25 cc.	Toluene 100 cc.	Benzene 100 cc.	Benzene 100 cc.	Benzene 100 cc.	Benzene 100 cc.	Ethyl ether 150 cc.
Temp. °C.	60°	25°	50°	80°	50°	50°	5°/36°
Time, Min.	200	60	1080	60	1080	1080	60/60
Amount of Product, g.	2.5	15.1	22	20	18	18	2.1
Yield, %	8.5%	59.5%	66%	80%	72%	50%	4.1%
M.P. °C.	146—8°	146—8°	134—8°	146—8°	196—8°	liquid	146—8°
Product Identity	Tetrakis (triphenyl-phosphite) nickel	Tetrakis (triphenyl-phosphite) nickel	Tetrakis (tri-p-methoxy-phenyl-phosphite) nickel	Tetrakis (triphenyl-phosphite) nickel	Tetrakis (tridecyl-phosphite) nickel	Tetrakis (diphenyldecyl phosphite) nickel	Tetrakis (triphenyl-phosphite) nickel

The utility of the compounds prepared by the method of the invention is discussed in detail hereinbelow.

5 The concentration of catalyst of the formulas given above in the cyclooligomerization reaction is suitably 0.001% to 10% by weight of the conjugated diolefin monomer and the preferred quantity is between 0.05% and 4% by weight. Excessive quantities of catalyst are not proportionately beneficial. Excellent results have been achieved at catalyst concentrations of 0.5%, 1.0%, and 1.5% with tetra-

10 kis(triphenylphosphite) nickel. Polymerization inhibitors which may be present if desired include phenol, catechol, *p*-tertiary-butyl catechol, resorcinol, hydroquinone, and other known compounds. Polymerization inhibitors may be removed from the diolefin, or reduced in quantity, by means 15 such as potassium hydroxide, prior to the reaction. If such inhibitors are present and are not removed, the amounts thereof may be between 0.001% and 4% based on the weight of the open-chain conjugated diolefin. It is 20 not unusual to find that amounts in this range have been added to materials such as butadiene to stabilize them during storage, and amounts, of *p*-tertiary butyl catechol in butadiene, between about 3 ppm (parts per million) 25 and 100 ppm have been used. Pressures between 1.4 kilograms per square centimeter gauge and 70 kilograms per square centimeter gauge are applicable, usually depending upon the temperature at which the reaction is conducted, suitably between 40°C. and 250°C., 30 the preferred temperature being between about 90°C. and 180°C. Vigorous agitation is of benefit, particularly at the higher temperatures. The time of reaction depends in large part upon 35 the temperature; suitable times are between 0.05 and 25 hours, and more desirably between 0.2 and 10 hours.

40 The reaction may be batch or continuous, and with or without a solvent. Backmixing of reaction mixture with newly introduced reactants is advantageous. Suitable solvents are paraffinic, cycloparaffinic, olefinic, cyclo-olefinic and aromatic hydrocarbons, including 45 benzene, toluene, petroluem naphtha, hexane, heptane, isooctane, cyclohexane, cyclopentane, cyclooctadiene, and similar materials. Other solvents known to be useful for similar reactions, such as tetrahydrofuran, are optional. 50 Most desirably, the only materials present in the reaction zone in substantial quantities are the diolefin monomer, the catalyst, and the products of reaction. In some cases, the catalyst is desirably dissolved in a solvent such as tetrahydrofuran or benzene before introduction 55 into the reaction zone.

60 The monomer useful according to the present invention is an open-chain conjugated diolefin or halogen-substituted diolefin. The preferred diolefin is 1,3 - butadiene or a mono-substituted 1,3 - butadiene. Such monosubsti-

tuted 1,3 - diolefins include 2 - methyl - 1,3 - butadiene (isoprene); 1,3 - pentadiene (piperylene); and 2 - chloro - 1,3 - butadiene (chloroprene). Other useful conjugated open chain diolefins include 2,3 - dichloro - 1,3 - butadiene; 70 phenyldiolefins and 2,3 - dimethyl - 1,3 - butadiene. The halogen-substituted conjugated open chain diolefins preferably have no more than one halogen atom substituted for hydrogen in each diolefin molecule. Mixed halogen 75 derivatives such as chloro-bromo-1,3-butadienes may be used. Other compounds which form cycloolefins having at least eight carbon atoms in the ring may also be used, an example being 2,4-hexadiene. 80

The diolefin should be relatively pure although it may comprise relatively small amounts of impurities inherently present such as water, monoolefins, 1,2-diolefins, carbonyl compounds, and acetylenes. Normally these 85 materials appear in amounts between about 10 ppm (parts per million) and 600 ppm. Excessive amounts of certain impurities react with the catalyst or are detrimental in other ways and if not removed, are wasteful of catalyst, for 90 example. The quantity of water in the diolefin monomer may be reduced by freezing, chemically, or by the use of dessicants or dehydrating agents such as calcium sulfate, calcium carbide, silica gel, calcium oxide, or others known in 95 the art. A water content as low as 5 ppm is readily achieved, although good results are obtained with larger amounts such as 100 ppm. Ferrous salts, thiosulfites or sulfites may be used to reduce peroxide compounds. 100

The reactor may be constructed of any usual material, including stainless steel and mild steel. In using these materials, it has been found that after a short period of use an 105 apparently polymeric film thinly coats or lines the reactor.

An example of a method of using the catalysts prepared according to the invention is as follows:

EXAMPLE 14

110 An autoclave was charged with 100 grams of butadiene and 1.5 grams of tetrakis(tri-*p*-methoxyphenylphosphite) nickel dissolved in benzene. The reactor, sealed, was heated to a temperature of about 125°C. for 45 minutes. 115 Of the butadiene introduced, 59% was converted to products. The approximate product analysis was 80% 1,5 - cyclooctadiene, 9% vinylcyclohexene, and 3% 1,5,9 - cyclododecatriene (CDT), the remainder being materials 120 having a boiling point above that of CDT.

The above example is illustrative of one utility of the catalytic compounds prepared by the method described herein. Also, see application No. 19420/61 Serial No. 971,755, filed 125 May 30, 1961, for similar examples. Using as the catalyst the complex bis(orthophenylene-bisdimethylphosphine) nickel,



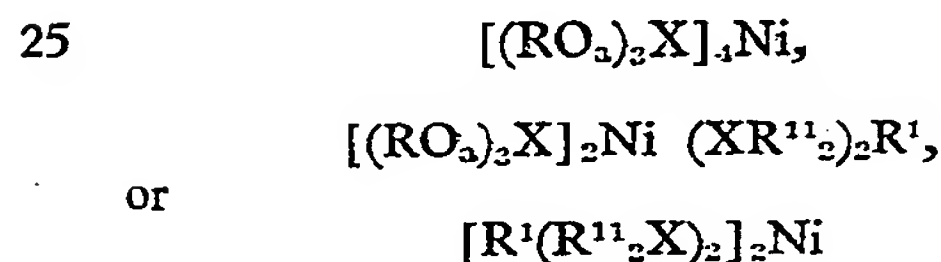
a catalyst concentration of 1% by weight based on butadiene, using a reaction time of three hours at a temperature of 150°C. and a pressure of 28 kilograms per square centimeter gage, is suitable to form oligomers of butadiene. The catalysts may be used with an activator, such as acetylene, isobutylene, or cyclooctadiene. Other suitable conditions are set forth above. Similar conditions are useful for trisubstituted complexes such as bis(triphenylphosphite) - orthophenylenebisdimethylphosphine nickel,



Another utility of the nickel compounds of the invention is in the preparation of metallic coatings on for instance, siliceous surfaces such as glass. By applying a thin coating of the compound to glass and thermally decomposing the complex in a vacuum or in a non-oxidizing atmosphere, coatings containing metallic nickel are obtained.

WHAT WE CLAIM IS:—

1. A method of preparing a nickel co-ordination compound of the formula:



wherein each of R, R¹ and R¹¹ is a hydrocarbon radical or an acyl or halogen derivative thereof, X is phosphorus, arsenic or antimony, and a is one or zero, which comprises reacting in an inert atmosphere (1) a nickel compound having a covalency or electrovalency of 2 or 3 with (2) a ligand or mixture of ligands of the formula



wherein R has the meaning given above for R, R¹ and R¹¹ and a is one or zero, in the presence of (3) a reducing agent selected from organometallic compounds, organometallic halides, metal hydrides, and organometallic hydrides, alkali metal ethoxides, metallic reducing agents more positive than nickel, hydrazine,

alkyl hydrazines, carbonyl hydrides, organic phosphines, organic phosphites and hydrogen.

2. A method according to claim 1, wherein the hydrocarbon radical is an aralkyl, cycloalkyl, aryl, alkaryl, arylalkyl, arylene or alkylene radical.

3. A method according to claim 1 or 2, in which the nickel compound is a nickel salt of an inorganic or carboxylic acid.

4. A method according to claim 3, in which the nickel compound is a nickel dihalide.

5. A method according to claim 1 or 2, in which the nickel compound is an organic chelate.

6. A method according to any preceding claim, in which the metallic reducing agent is lithium, sodium, potassium, magnesium, calcium, barium, zinc, cadmium, iron or aluminium.

7. A method according to any preceding claim, in which a hydrocarbon solvent is included in the reaction mixture.

8. A method according to any preceding claim, in which the molar ratio of phosphorus, arsenic or antimony to nickel is between 4:1 and 20:1.

9. A method of preparing a nickel co-ordination compound as defined in claim 1, as herein described and with reference to Nos. 1—13 of the foregoing Examples.

10. A nickel co-ordination compound, when prepared according to the method of any preceding claim.

11. A method of cyclooligerimizing an open-chain conjugated diolefin or halogen-substituted diolefin, in which a nickel co-ordination compound according to claim 10 is used as catalyst.

12. A method of cycloligerimizing an open chain conjugated diolefin or halogen-substituted diolefin, as hereinbefore described and with reference to No. 14 of the foregoing Examples.

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Reference has been directed in pursuance of Section 9, subsection (1) of the Patents Act, 1949, to patent No. 882,400.

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